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13. ABSTRACT (Maximum 200 words) For this project number of new polymer materials were synthesized including trifunctional, tetrafunctional and hexafunctional regular graft copolymers. Additionally, a range of poly(cyclohexadiene) (PCHD) homopolymers and block copolymers containing PCHD blocks were prepared. The morphologies of the regular graft copolymers, and PCHD containing block copolymers were determined by TEM and SAXS. Additionally, the morphologies of cyclic block copolymers were studied and compared to their linear analogs. The tensile mechanical properties of the regular multigraft materials were studied and related to molecular architecture. It was found that increasing junction point functionality and increasing number of junction points per molecule increased strength and toughness, and decreased hysteresis. A series of block double graft (BDG) copolymers of unique molecular architecture were studied to relate molecular architecture to morphology and mechanical properties. The mechanical properties of some BDG materials compared favorably to commercial thermoplastic elastomers.				
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(1) Forward

For this project number of new polymer materials were synthesized including trifunctional, tetrafunctional and hexafunctional regular graft copolymers. Additionally, a range of poly(cyclohexadiene) (PCHD) homopolymers and block copolymers containing PCHD blocks were prepared. The morphologies of the regular graft copolymers, and PCHD containing block copolymers were determined by TEM and SAXS. Additionally, the morphologies of cyclic block copolymers were studied and compared to their linear analogs. The tensile mechanical properties of the regular multigraft materials were studied and related to molecular architecture. It was found that increasing junction point functionality and increasing number of junction points per molecule increased strength and toughness, and decreased hysteresis. A series of block double graft (BDG) copolymers of unique molecular architecture were studied to relate molecular architecture to morphology and mechanical properties. The mechanical properties of some BDG materials compared favorably to commercial thermoplastic elastomers.

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(4) Statement of the Problem Studied

This research project aimed to develop new methods to synthesize block and graft copolymer materials of novel controlled chemistry and molecular architecture. Additionally, the influence of this molecular architecture on morphology and properties was studied. The properties studies focused mostly on tensile mechanical properties.

(5) Summary of Most Important Results

5.1 Synthesis of Regular Multigrafts:

A large number of poly(isoprene-graft-styrene) copolymers with multiple, regularly spaced branch points were synthesized for this project. The synthetic strategy employs classical anionic polymerization techniques and utilizes a modular approach in which polystyryllithium and α,ω -poly(1,4-)isoprenyl dilithium are sequentially incorporated into chlorosilane linking centers. Previous syntheses have afforded graft copolymers with trifunctional (“combs”) and tetrafunctional (“centipedes”) branch points. Under this grant we extend this methodology to include a novel regular multigraft material with hexafunctional branch points (“barbwires”). These materials possess polystyrene side chains of uniform length attached in clusters of four at regularly spaced points along a narrow molecular weight distribution polyisoprene main chain. In the synthesis of barbwires, PSLi is added first to 1,6-bis(trichlorosilyl)hexane, in an incremental fashion, until 4 equivalents have been incorporated to the linking silane; LiPILi is next added in a slight stoichiometric excess, resulting in a condensation between macromolecular dinucleophiles and dielectrophiles. Homogenous multigraft samples of all three architectures were synthesized, with a polydispersity index of 1.2, through fractionation of the raw condensation products. The three architectures are depicted in Figure 1.

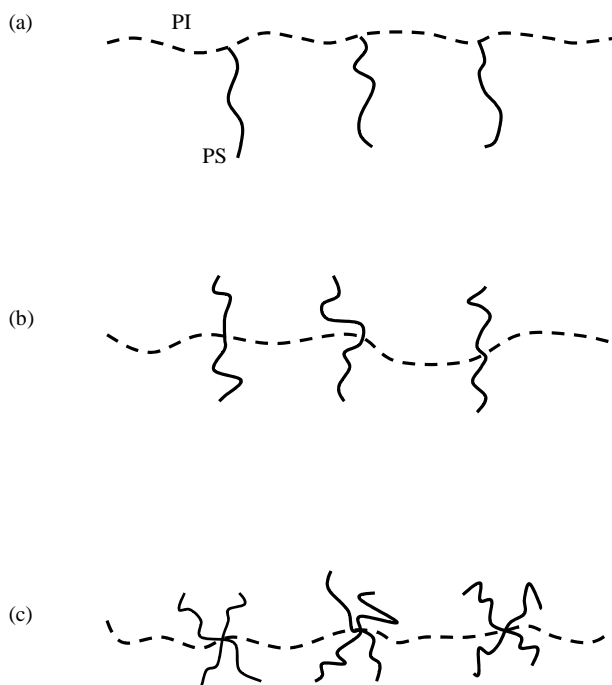
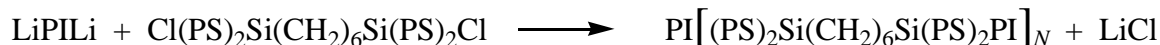


Figure 1. Regular multigraft poly(isoprene-graft-styrene) architectures:
(a) $A(BA)_N$ “comb,” (b) $A(B_2A)_N$ “centipede,” (c) $A(B_4A)_N$ “barbwire.”

The synthetic strategy is basically the same for each species: the branches and connectors are made separately by anionic polymerization, chlorosilane chemistry is used to functionalize (join, if desired) polystyrene branch segments, and then condensation of the

resulting dichlorosilane macromonomer with α,ω -dianionic poly(isoprene) (backbone segment) is carried out. For example, the barb wire synthesis scheme is shown below.



This last step is a condensation polymerization meaning that the final product contains species differing in number of branch points but having the same branch lengths and connector lengths. Fractionation of this product yields narrow MWD fractions varying in number of branch points but having the same composition.

The molecular characteristics of the combs, centipedes, and barb wire molecules synthesized for this project are summarized in the following tables.

Table 1. Multigraft Series, Molecular Weight Characteristics Summary

Synthesis	PS Graft	PI Spacer	Unit	Multigraft		
Project	$M_w (\times 10^{-3})$	$M_w (\times 10^{-3})$	$M_w (\times 10^{-3})$	$M_w (\times 10^{-3})$	%PS	Graft Pts.
MG3 1	9.5	105.0	115	601	6.1	4.3
				406	6.1	2.6
				316	5.9	1.8
MG3 2	31.6	86.0	118	515	18.4	3.7
				391	19.0	2.6
				315	19.0	2.0
MG3 3	60.3	48.0	108	464	44.6	3.8
				400	47.5	3.3
				360	48.5	2.9
MG3 4	77.3	34.2	112	421	65.4	3.5
				338	67.2	2.7
				268	67.8	2.1
MG3 5	79.5	23.6	103	382	82.2	3.5
				291	82.4	2.6
				—	—	—
MG4 1	11.1	97.2	119	691	15.2	5.5
				475	15.1	3.5
				372	15.1	2.5
MG4 2	16.8	87.6	121	891	24.9	6.6
				624	24.7	4.4
				472	24.5	3.2
MG4 3	26.6	63.6	117	930	43.5	7.4
				681	43.7	5.3
				572	43.9	4.4
MG6 1	8.2	86.8	120	705	23.5	5.2
				515	23.2	3.6
				411	23.1	2.7
MG6 2	13.0	63.3	115	409	38.3	3.0
				328	37.9	2.3
				287	38.2	1.9

Table 2. Multigraft Complete Series, Compositional Characterization

Multigraft		Measured, mass% PS		Calculated PS Mass %
Sample		¹ H NMR	SEC-UV	
MG3 1	fraction 1	6.1	7.4	6.8
	fraction 2	6.1	7.2	6.2
	fraction 3	5.9	7.1	5.5
MG3 2	fraction 1	18.4	19.8	22.4
	fraction 2	19.0	19.9	21.0
	fraction 3	19.0	20.2	19.5
MG3 3	fraction 1	44.6	45.0	49.9
	fraction 2	47.5	47.9	49.0
	fraction 3	48.5	49.8	48.3
MG3 4	fraction 1	65.4	65.0	63.7
	fraction 2	67.2	66.9	62.3
	fraction 3	67.8	67.1	60.5
MG3 5	fraction 1	82.2	81.5	72.4
	fraction 2	82.4	81.7	70.9
	fraction 3	—	—	—
MG4 1	fraction 1	15.2	16.5	17.6
	fraction 2	15.1	16.6	16.3
	fraction 3	15.1	16.1	15.1
MG4 2	fraction 1	24.9	26.6	25.0
	fraction 2	24.7	25.7	23.8
	fraction 3	24.5	25.6	22.6
MG4 3	fraction 1	43.5	44.5	42.4
	fraction 2	43.7	44.7	41.3
	fraction 3	43.9	44.5	40.5
MG6 1	fraction 1	23.5	24.7	24.0
	fraction 2	23.2	24.5	22.8
	fraction 3	23.1	24.3	21.6
MG6 2	fraction 1	38.3	39.0	38.1
	fraction 2	37.9	38.9	36.4
	fraction 3	38.2	39.1	35.2

5.2 Morphology of Regular Multigraft Block Copolymers

The morphologies of the regular multigraft samples listed in Tables 1 and 2 were determined using TEM and SAXS. The results are summarized in Table 3. Figure 2 shows TEM images of three fractions of a barbwire architecture with 5.2, 3.6, and 2.7 graft points per molecule. All these samples have PS volume fractions of 20.9. Depending upon the number of branch points per molecule these materials either form microphase separated lamella or a microphase separated but disordered structure. Based on the structure per junction point (constituting block copolymer) and the Milner morphology diagram, which has underpinned our morphological investigations of these materials, these materials are expected to form a lamellar morphology. As was found in our studies of similar multigraft materials with tetrafunctional branch points (Fig. 1b), as the number of branch points per molecule increases, the ability to form long range order is dramatically reduced. The sample with 2.7 junction points per molecule forms a fairly well ordered lamellar morphology. The sample with 3.6 junction points per molecule forms a morphology with is much less ordered and just barely recognizable as lamellar. The sample with 5.2 junction points per molecule forms a microphase separated structure with no discernable lamellar structure or long range order.

Table 3: Morphological Results for Regular Multigraft Copolymers

Sample	Structure	Vol% PS	q^* (\AA^{-1})	higher order reflections	$2\pi/q^*$ (nm)	Morphology
MG6-1						
Fraction 1	$-(I_2S_4)_n-$	20.9	0.01851		33.9	random
Fraction 2	$-(I_2S_4)_n-$		0.01851			random + Lamellae
Fraction 3	$-(I_2S_4)_n-$		0.01851			Lamellae
MG6-2						
Fraction 1	$-(I_2S_4)_n-$	35.2	0.01355	0.03061	46.4	Lamellae
Fraction 2	$-(I_2S_4)_n-$		0.01424	0.02920	44.1	Lamellae
Fraction 3	$-(I_2S_4)_n-$		0.01638	0.03204	38.4	Lamellae
MG4-1						
Fraction 1	$-(I_2S_2)_n-$	13.5	0.02207		28.5	disordered PS spheres
Fraction 2	$-(I_2S_2)_n-$		0.02207		28.5	disordered PS spheres
Fraction 3	$-(I_2S_2)_n-$		0.01994		31.5	disordered PS spheres
MG4-2						
Fraction 1	$-(I_2S_2)_n-$	22.2	0.01994		31.5	PS cylinders
Fraction 2	$-(I_2S_2)_n-$		0.01994		31.5	PS cylinders
Fraction 3	$-(I_2S_2)_n-$		0.01851		33.9	PS cylinders
MG4-3						
Fraction 1	$-(I_2S_2)_n-$	40.7	0.01567		40.1	Lamellae
Fraction 2	$-(I_2S_2)_n-$					Lamellae
Fraction 3	$-(I_2S_2)_n-$					Lamellae

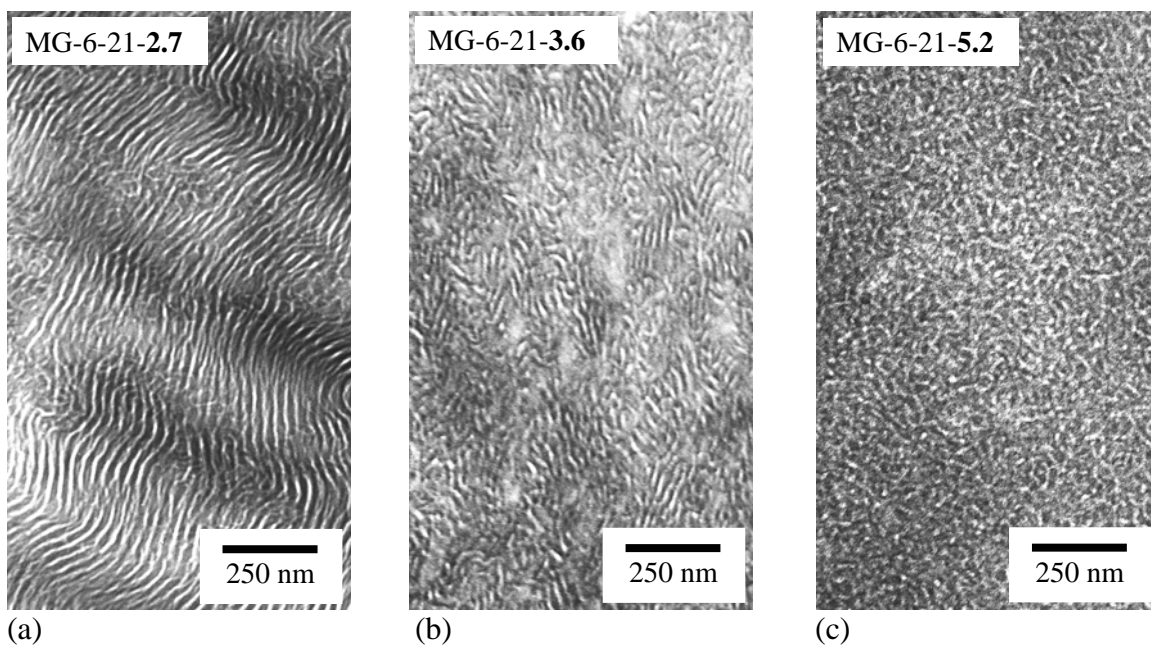


Figure 2: TEM images of hexafunctional multigraft materials with 21 vol. % PS and on average 2.7 (a), 3.6 (b), and 5.2 (c) graft points per molecule.

5.3 Mechanical Properties of Regular Multigraft Block Copolymers

The mechanical properties of the regular multigraft copolymers have been studied. Figure 3 compares the stress vs. strain behavior of 5 branch point 21 vol. % PS multigraft materials with tetrafunctional and hexafunctional branch points. In this comparison the two materials are identical in composition and in number of branch points per molecule. The only difference is in branch point functionality: Fig. 1b vs. Fig. 1c. The hexafunctional junction points result in an approximately 2.5x increase in strength with a modest about 20% reduction in ultimate strain. These results indicate that the hexafunctional junction points provide significantly more robust mechanical reinforcement than do the tetrafunctional branch points.

Figure 4 compares the stress vs. strain behavior of 21 vol. % PS multigraft materials with an average of 2, 3, and 5 hexafunctional branch points per molecule. Clearly increasing the number of hexafunctional junction points results in an increase in strength with little loss in extensibility. These trends are similar to those reported and published earlier for multigraft copolymers with tetrafunctional junction points (Fig. 1b).

Figure 5 shows hysteresis studies of tetrafunctional multigrafts as a function of number of junction points. Samples were strained to 500%, allowed to relax, and the residual strain observed. Increasing the number of junction points per molecule reduces the size of the hysteresis loop and the amount of residual strain. Low hysteresis is an advantage for these materials in potential Army elastomer applications. Commercial thermoplastic

elastomers, such as Kratons, display higher hysteresis than the 10 branch point material reported in Figure 5.

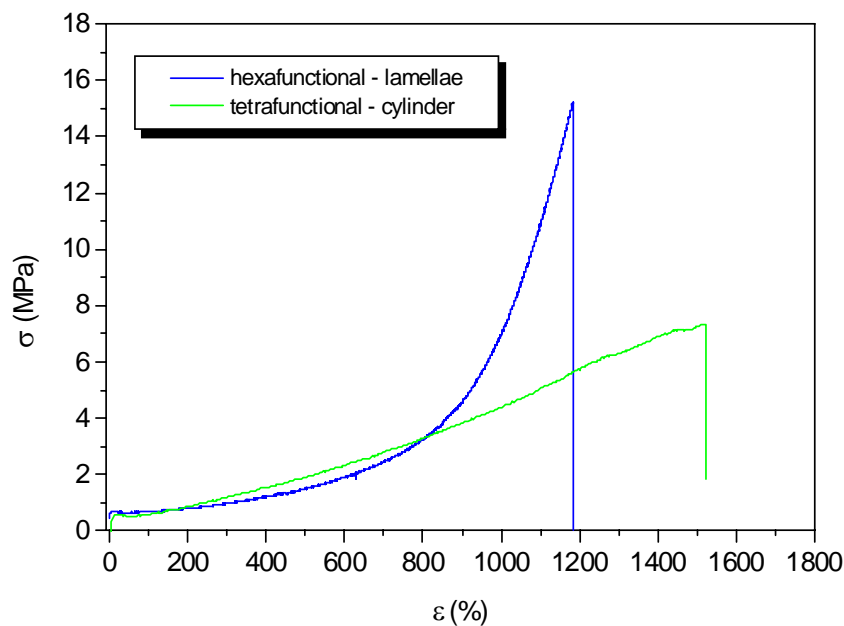


Figure 3: Comparison of stress vs. strain behavior of 5 branch point 21 vol. % PS multigraft materials with tetrafunctional and hexafunctional branch points.

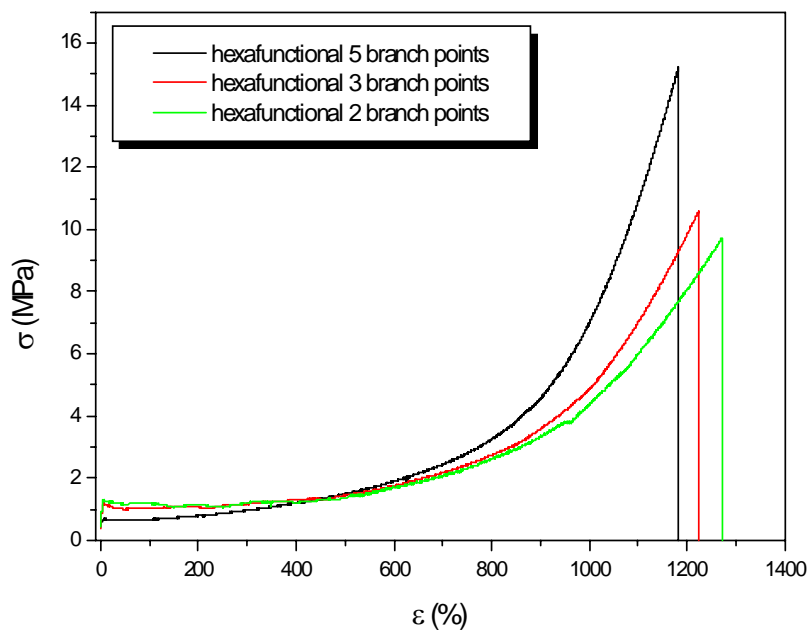


Figure 4: Comparison of stress vs. strain behavior of 21 vol. % PS multigraft materials with an average of 2, 3, and 5 hexafunctional branch points per molecule.

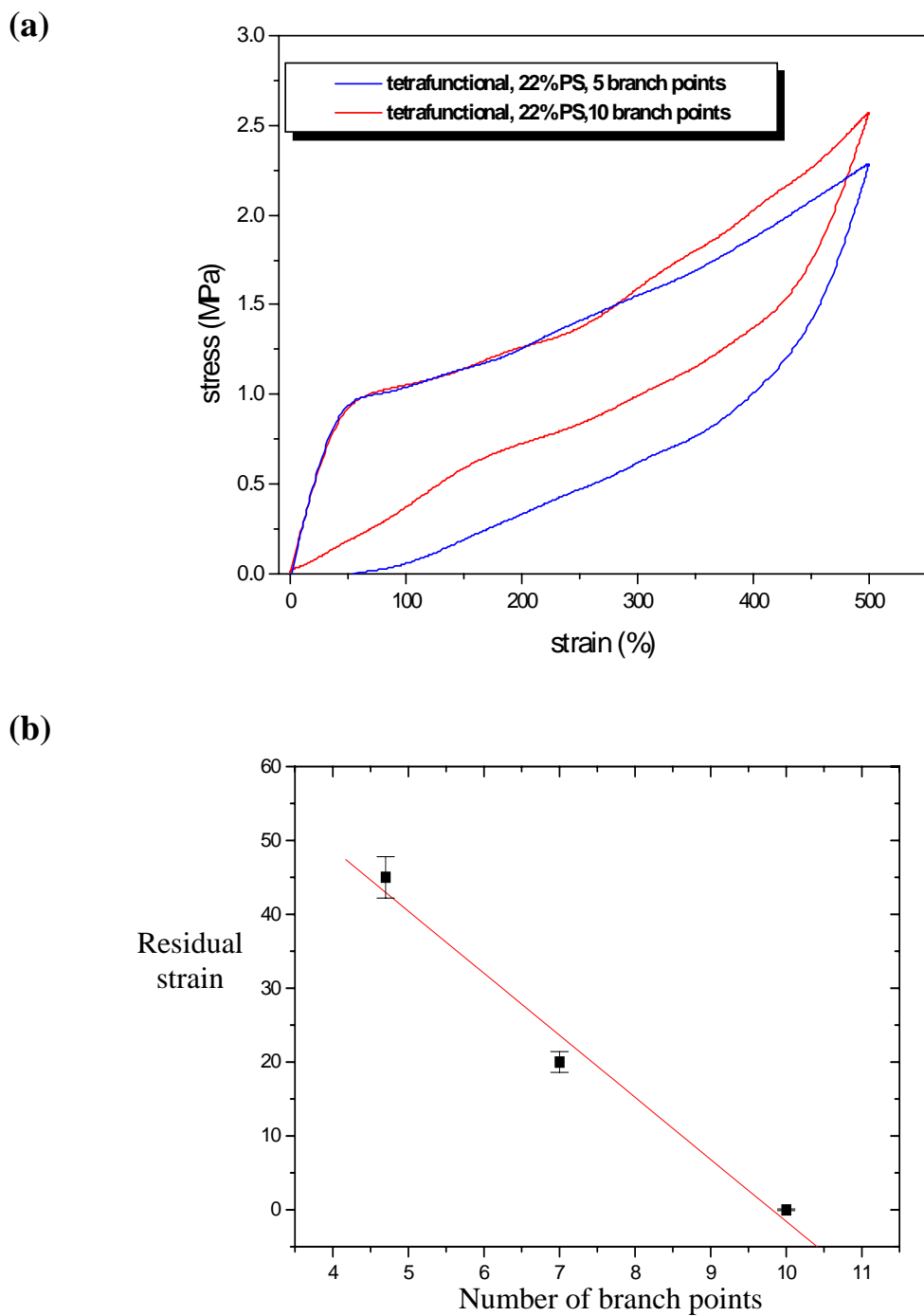


Figure 5: Hyseresis studies of tetrafunctional multigrafts as a function of number of junction points. (a) stress vs. strain curves. (b) residual strain as a function of number of junction points.

5.4 Block Double Graft Block Copolymers

Morphological characteristics and mechanical properties of a series of block-double-graft (BDG) copolymers and terpolymers polystyrene-[1,2-polybutadiene-*g*-X₂] (X = 1,4-polybutadiene, 1,4-polyisoprene, polystyrene, and polystyrene-*b*-1,4-polyisoprene diblocks) were investigated by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and tensile testing. The molecular architectures for these materials are shown in Table 4. These materials were obtained from the group of Prof. Hadjichristidis at the University of Athens. All BDG materials have linear polystyrene-1,2-polybutadiene (PS-*b*-1,2-PBD) diblock copolymer backbones. Two identical branches are grafted at every randomly distributed tetrafunctional junction point on the 1,2-PBD part of the backbone.

As listed in Table 5, classical microstructures, such as BCC spheres, HEX cylinders and lamellae, are obtained at different total PS volume fractions. It is found that when the branches are polydienes, the BDG molecules yield the same morphologies as their linear diblock counterparts. In such cases, phase separation occurs between the polystyrene and a combined diene microdomain formed by backbone 1,2-PBD and the polydiene branches. In BDG materials in which the branches are polystyrene-polyisoprene diblock copolymers, lamellae are obtained at a total PS volume fraction close to 0.50. Lamellar long periods of these BDG terpolymers increase with increasing molecular weights of the PS-PI branches and with decreasing number of junction points along the 1,2-PBD backbone.

These BDG materials are similar in their molecular architecture to the multigrfts (Fig. 1) except that they have blocks of PS attached at one end of the backbone. Additionally for architectures BDG 6 and BDG 7 the grafts themselves are PS-PI diblock copolymers. The morphological and mechanical test results on these block double graft materials has been published in: *Zhu, Y., Weidisch, R., Gido, S. P., Velis, G., Hadjichristidis, N. Macromolecules* **2002**, 35, 5903. The mechanical results are summarized in the Figure 6.

Table 4: Block Double Graft Molecular Architectures

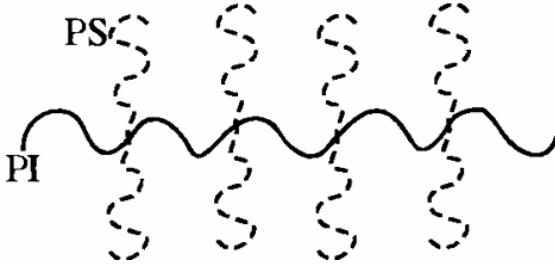
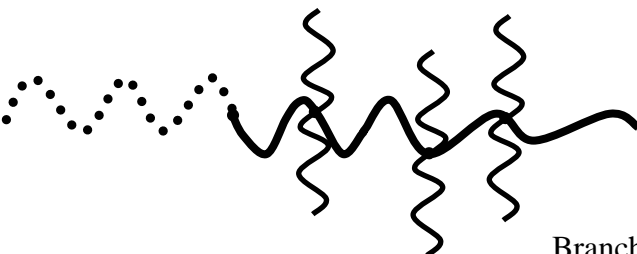
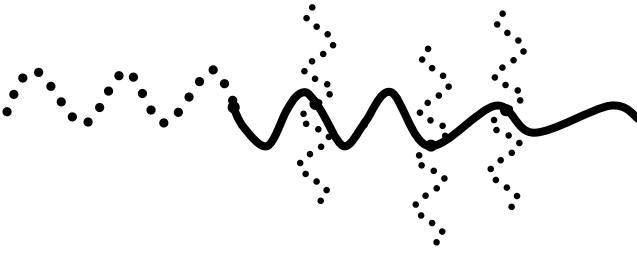
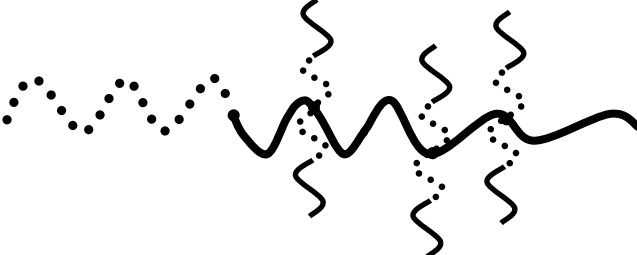
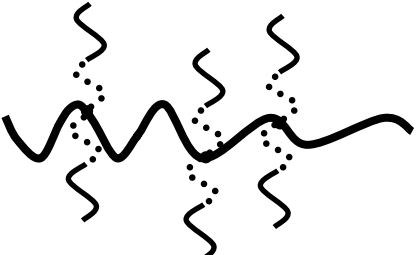
PI-g-PS ₂	
BDG 1, 2, 3, 4	 <p>Branches = 1,4-PBD or PI</p>
BDG 5	 <p>Branches = PS</p>
BDG 6, 7	 <p>Branches = PS-PI</p>
HDG	 <p>Branches = PS-PI</p>

Table 5: Block Double Graft Copolymer Morphological Results

Sample		Morphology	d^* (Å) ^a	Vol% PS	Vol% PBD	Vol% PI
BDG ₁	PS-[1,2-PBD- <i>g</i> -(1,4-PBD) ₂]-1	PS Cylinders	381	22.5	77.5	
BDG ₂	PS-[1,2-PBD- <i>g</i> -(1,4-PBD) ₂]-2	PS Spheres	230	12.6	87.4	
BDG ₃	PS-[1,2-PBD- <i>g</i> -(1,4-PBD) ₂]-3	PS Cylinders	335	27.0	73.0	
BDG ₄	PS-[1,2-PBD- <i>g</i> -(PI) ₂]	Random PS Spheres	268	7.60	5.30	87.1
BDG ₅	PS-[1,2-PBD- <i>g</i> -(PS) ₂]	Disordered		89.2	10.8	
BDG ₆	PS-[1,2-PBD- <i>g</i> -(PS-PI) ₂]-1	Lamellae	175	48.8	5.70	45.5
BDG ₇	PS-[1,2-PBD- <i>g</i> -(PS-PI) ₂]-2	Lamellae	244	44.9	7.10	48.0
HDG	1,2-PBD- <i>g</i> -(PS-PI) ₂	Lamellae	167	41.9	7.7	50.4

^a Primary SAXS reflection, $d^* = 2\pi/q^*$.

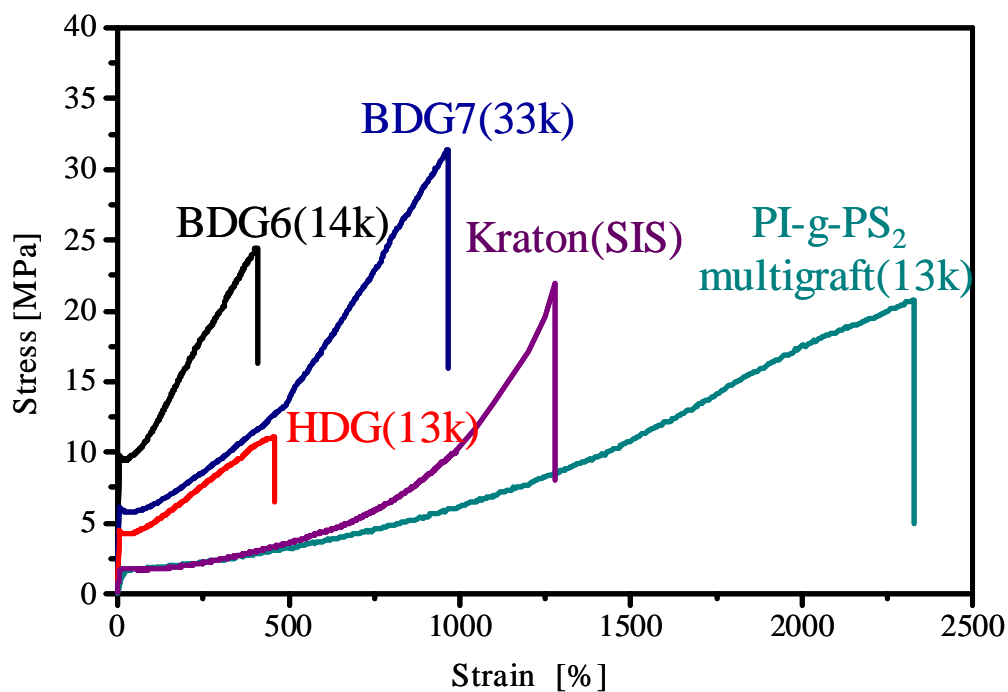


Figure 6: Stress-Strain curves for (1) BDG6, 9 PS-PI branches, and the branch molecular weight is 14,000 g/mol; (2) BDG7, 3 PS-PI branches, and the branch molecular weight is 32,800 g/mol; (3) HDG, 9 PS-PI branches, and the branch molecular weight is 12,500 g/mol; (4) Kraton[®]; (5) PS-*g*-PI₂ multigraft copolymer with 9 PS branches at branch molecular weight of 13,000 g/mol.

The curve labeled PI-g-PS₂ is a tetrafunctional multigraft material for which results were published previously [*Macromolecules*, 34, 6333 (2001)]. It is included for comparison, as is the curve for the commercial Kraton material. Data is shown for two block double graft (BDG) materials with the BDG 6-7 architecture in the table above. While these materials have less extensibility, than the tetrafunctional multigraft, they have significantly higher strength. The lower strength HDG architecture lacks the PS block attached to the backbone.

The unusual strength of the block double graft materials is possibly due to the fact that their molecular architecture can result in chain conformations that bridge three reinforcing PS domains. Molecules in conventional triblock thermoplastic elastomers such as the Kraton can only bridge two reinforcing domains.

For BDG terpolymers, we found two parameters that can adjust material properties - molecular weight of the branches and molecular architecture. Branches must exceed the entanglement molecular weight in order to provide effective physical crosslinks. In terms of molecular architecture, the presence of PS block on polymeric backbone provides an extra coupling point between PS and rubbery domains, which appears to enhance properties. The number of junction points and the functionality of these junction points are also very important aspects for energy transfer between different domains if chain entanglement can be achieved in such materials.

5.5 Synthesis of Model Linear Co-, Ter- and Quaterpolymers containing Styrene, Butadiene, Isoprene and 1,3-Cyclohexadiene

The synthesis of model linear co-, ter- and quaterpolymers containing styrene, butadiene, isoprene and 1,3-cyclohexadiene (CHD) was achieved by sequential anionic polymerization. 1,3-cyclohexadiene was the last monomer added, in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) giving polycyclohexadiene with 1,2 microstructure predominate (1,2-PCHD), or in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) giving PCHD with 1,4 microstructure predominate (1,4-PCHD). Extended characterization was carried out by size exclusion chromatography, membrane osmometry, low and multi angle laser light scattering, laser differential refractometry and ¹H-NMR spectroscopy. The results are summarized in Tables 6-8 below. Solubility differences between copolymers having 1,2-PCHD and 1,4-PCHD were observed, as only the block copolymers with high 1,2-content formed micelles in THF.

By using DABCO and TMEDA as additives for the controlled anionic polymerization of 1,3-cyclohexadiene and by sequential addition of monomers, model co-, ter- and quaterpolymers were successfully synthesized and characterized. The microstructure of polycyclohexadiene in the presence of DABCO was high 1,4 while with TMEDA the 1,2 microstructure was predominate (~55 wt %), producing poly(cyclohexadienes) with different solution properties. All materials with only 1,2-PCHD formed micelles in THF. New very interesting terpolymers containing three different dienes (PB-*b*-PI-*b*-PCHD)

and elastomer terpolymers with polystyrene and polycyclohexadiene as the outer blocks and polybutadiene as the middle block (PS-*b*-PB-*b*-PCHD) were also prepared.

Table 6. Molecular characteristics of diblock copolymers of 1,3-Cyclohexadiene (CHD) with Styrene, Butadiene and Isoprene

Sample	First Block		Diblock Copolymer		
	$M_w^b \times 10^{-3}$ (g/mol)	M_w/M_n^c	$M_n^d \times 10^{-3}$ (g/mol)	M_w/M_n^c	PCHD ^f (wt %)
PS- <i>b</i> -(1,4-PCHD) ^a	21.4 ^c	1.03	40.2	1.12	55
PS- <i>b</i> -(1,2-PCHD)	21.4 ^c	1.03		1.21	50
PB- <i>b</i> -(1,4-PCHD)	22.5	1.03	42.5	1.16	62
PB- <i>b</i> -(1,2-PCHD)	22.5	1.03		1.20	53
PI- <i>b</i> -(1,4-PCHD)	29.0	1.06	51.2	1.19	60
PI- <i>b</i> -(1,2-PCHD)	21.7	1.15		1.27	54

^a Diblock copolymer with PS as the first block and PCHD as the second having 1,4 microstructure predominate.

^b LALLS in THF at 25 °C. ^c SEC in THF at 30 °C calibrated with polystyrene standards.

^d M_n by membrane osmometry in toluene at 37 °C. ^e MALLS in CHCl₃ at 25 °C. ^f ¹H-NMR in CDCl₃ at 30 °C.

Morphological studies of some of the block copolymers containing PCHD blocks confirmed the presence of a previously reported, and highly unusual, core shell cylinder morphology.[*Macromolecules* **1999**, 32, 3216] A reason postulated for the formation of this structure was the possibility that the PCHD blocks are quite rigid. In order to gain more data on this issue a number of PCHD homopolymers were synthesized and studied. Homopolymers of PCHD, as well as well-defined block copolymers, terpolymers, and quaterpolymers with styrene, butadiene, and isoprene, were synthesized by anionic polymerization. By choice of initiator system, the microstructure of the PCHD could be adjusted to have either 50% 1,4- microstructure or 95% 1,4- microstructure. The microstructure of the PCHD has a large impact on the glass transition temperature of the polymer.

Table 7. Molecular characteristics of linear terpolymers of 1,3-Cyclohexadiene (CHD) with Styrene, Butadiene and Isoprene

Sample	First Block		Diblock			Terpolymer		
	$M_w^b \times 10^{-3}$	M_w/M_n^c	$M_w^b \times 10^{-3}$	M_w/M_n^c	First block ^d	$M_n^e \times 10^{-3}$	$M_w^f \times 10^{-3}$	M_w/M_n^c
	(g/mol)		(g/mol)		(wt %)	(g/mol)	(g/mol)	
PS- <i>b</i> -PB- <i>b</i> -(1,4-PCHD) (17/43/40) ^a	4.6 ^c	1.03		1.04	28	29.0		1.05
PS- <i>b</i> -PB- <i>b</i> -(1,2-PCHD) (17/43/40)	4.6 ^c	1.03		1.04	28			1.06
PS- <i>b</i> -PB- <i>b</i> -(1,4-PCHD) (34/32/34)	11.0	1.05	22.5	1.03	49	33.5	36	1.09
PS- <i>b</i> -PB- <i>b</i> -(1,2-PCHD) (32/28/40)	11.0	1.05	22.5	1.03	49	45.5		1.07
PB- <i>b</i> -PS- <i>b</i> -(1,4-PCHD) (17/34/49)	8.0	1.03		1.07	34	39.0		1.12
PB- <i>b</i> -PI- <i>b</i> -(1,4-PCHD) (25/29/46)	11.0	1.03	24.5	1.04	44	38.0		1,10
PB- <i>b</i> -PI- <i>b</i> -(1,2-PCHD) (32/39/29)	11.0	1.03	22.6	1.05	48			1.09

^a Terpolymer with PS as the first block, PB as the second and PCHD as the third having 1,4 microstructure predominate. In brackets is the wt % composition by ¹H-NMR in CDCl₃ at 30 °C. ^b LALLS in THF at 25 °C. ^c SEC in THF at 30 °C calibrated with polystyrene standards. ^d ¹H-NMR in CDCl₃ at 30 °C. ^e M_n by membrane osmometry in toluene at 37 °C. ^f MALLS in CHCl₃ at 25 °C.

Table 8. Molecular characteristics of linear quaterpolymers of 1,3-Cyclohexadiene (CHD) with Styrene, Butadiene and Isoprene

Sample	First Block		Diblock		First block ^c (wt %)	Terpolymer			Quarter-polymer	
	M_w^a $\times 10^{-3}$	M_w/M_n^b	M_w^a $\times 10^{-3}$	M_w/M_n^b		M_w^a $\times 10^{-3}$	M_w/M_n^b	Composition ^c (wt %)	M_n^d $\times 10^{-3}$	M_w/M_n^b
	(g/mol)		(g/mol)			(g/mol)			(g/mol)	
PS- <i>b</i> -PB- <i>b</i> -PI- <i>b</i> -(1,4-PCHD) (19/20/22/39)	13.1	1.03	26.2	1.05	50	39.1	1.10	33/33/34	52.6	1.14
PS- <i>b</i> -PB- <i>b</i> -PI- <i>b</i> -(1,2-PCHD) (15/16/18/51)	13.1	1.03	26.2	1.05	50	36.5	1.07	34/34/32		1.15
PS- <i>b</i> -PB- <i>b</i> -(1,4-PCHD)- <i>b</i> -PI	27.5 ^d	1.03	56.0 ^d	1.03	49	60.0 ^d	1.07	43/47/10	197	1.08

^a LALLS in THF at 25 °C. ^b SEC in THF at 30 °C calibrated with polystyrene standards. ^c ¹H-NMR in CDCl₃ at 30 °C. ^d M_n by membrane osmometry in toluene at 37 °C. ^e MALLS in CHCl₃ at 25 °C.

Table 9. Characteristics of PCHD homopolymers

Run	Sample	M_n (Kg/mol)	PDI	1,4/1,2 (NMR)	T _g (°C)
1	KH6-129A	2.3	1.10	95/5	71.5
2	KH6-129B	4.4	1.08	95/5	83.1
3	KH6-129C	8.7	1.04	95/5	94.2
4	KH6-129D	12.4	1.05	95/5	102.5
5	KH6-129E	17.9	1.09	95/5	117.3
6	KH6-132A	2.6	1.11	50/50	79.2
7	KH6-132B	6.1	1.06	51/49	94.7
8	KH6-132C	15.7	1.07	51/49	131.9
9	KH6-132D	23.6	1.09	49//51	147.0

PCHD is of interest in part because of its high glass transition temperature (Figure 7), which is further increased to 200 - 250°C upon hydrogenation. Thermoplastic elastomers containing hydrogenated PCHD end blocks and low T_g hydrogenated PI mid-blocks should be outstanding thermoplastic elastomers with unequaled thermo-oxidative stability. Therefore the thermal stability of these materials was investigated.

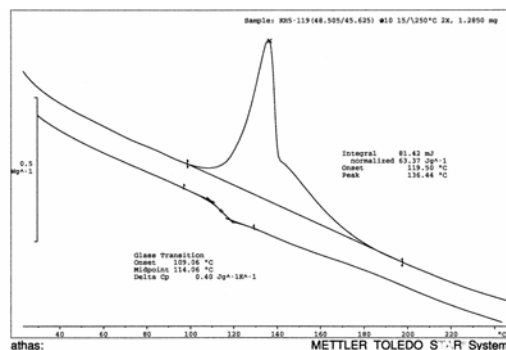


Figure 7 DSC traces of a PCHD sample (1st run and 2nd run)

Interestingly, PCHD shows a strong exothermic peak on first heating in DSC. This suggests the presence of formation of higher order structures (liquid crystals?) or perhaps partial crystallization. The exotherm is far too strong to reflect stress release in the material. These results should be further investigated as they could explain the unusual solubility of PCHD.

Weight loss at low temperature (ca. 120°C) is observed in TGA (Figure 8).

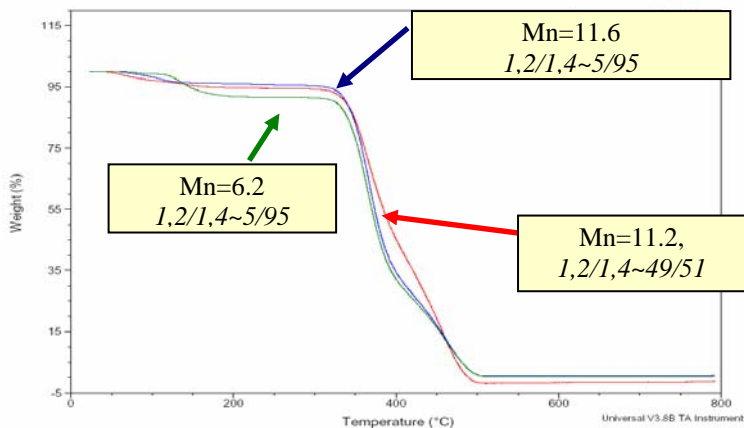


Figure 8. TGA traces of PCHD various samples

It was found that the initial weight loss is dependent of molecular weight, the lower the molecular weight, the higher the weight loss (Figure 8). TGA-MS revealed that the main fragments during the initial degradation were around 56 and 80 which corresponding to butyl group and the monomer unit. When the samples were treated under Argon at 200°C, we did not see the initial weight loss below 350 °C (Figure 9). However, NMR spectra did show the changes in the alkyl region (Figure 10). It is very difficult to assign all the peaks, but the ratios of protons from unsaturated carbon to those from the saturated carbon changed. After treatment, the polymer did not dissolve in CHCl_3 completely, which indicated crosslinking occurred.

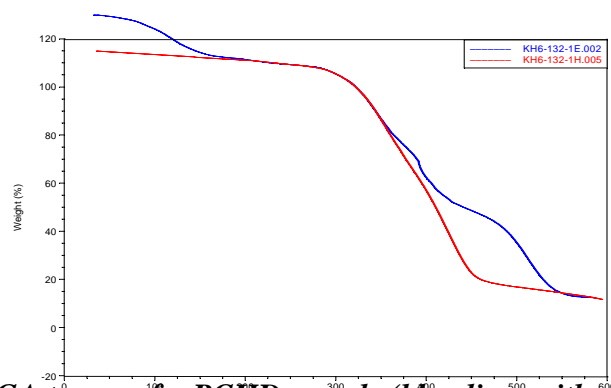


Figure 9. TGA traces of a PCHD sample (blue line: without treatment, red line: after treat at 200°C for 30 min)

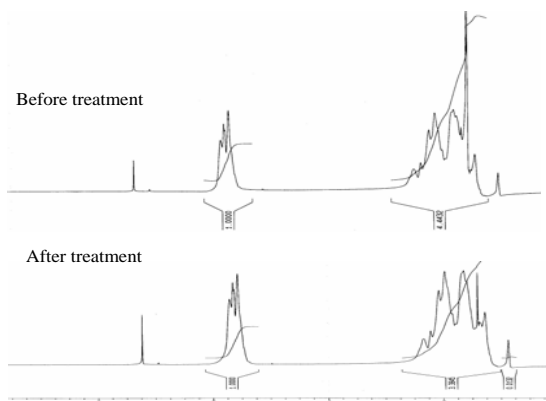


Figure 10. ^1H -NMR spectra of a PCHD sample before treatment and after treatment at 200°C for 30 min (obtained in CDCl_3)

At higher temperature ($>350^\circ\text{C}$), the decomposition occurred in two stages. The first stage is faster for high 1,4/1,2 ratio sample than that for lower 1,4/1,2 ratio sample. When the temperature reached around 380°C , the processes reversed. There was some residual left for higher 1,4 PCHD samples, even at 800°C . Those residual were amorphous carbon as confirmed by Raman spectrum (Figure 11). The two processes might be crosslinking and carbonation. Detailed studies of these transitions are under way.

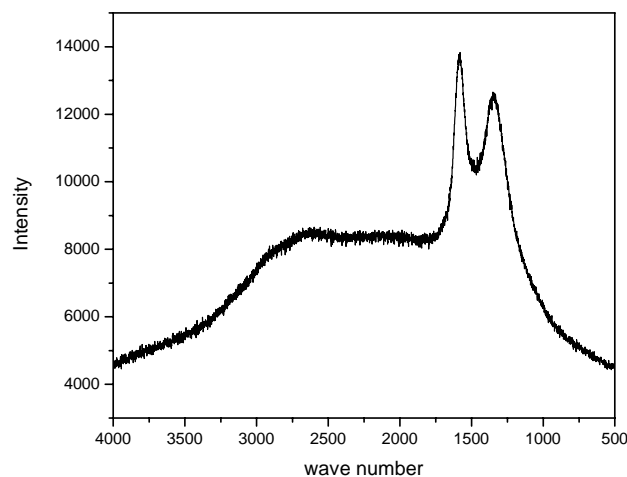


Figure 11. Raman spectrum of a TGA residual (800 °C) for a PCHD sample

Attempts have also been made to probe the conformational characteristics of PCHD having high 1,4 microstructure. Attempts to measure the radius of gyration by light scattering failed because the size was too small to yield a measurable angular dependence. However, these data interestingly show that THF is a worse than theta solvent for PCHD at both 40 and 50°C, as reflected in the negative second virial coefficients (Table 10).

Table 10: Results from Static Light Scattering on PCHD

Sample	M_w	A_2^*	M_w	A_2^*
	40 °C		50 °C	
KH5-162	18500	-3.0	18500	-1.7
KH5-127	17100	-4.0		
KH5-167	11700	-3.7	11800	-2.6
In THF * units of $10^{-4} \text{mol g}^{-2} \text{cm}^3$				

Intrinsic viscosity measurements (Table 11) conducted on these same materials allowed us to estimate the persistence length using the wormlike chain model (Yoshizaki et al. *Macromolecules* (1988)). These data indicate a persistence length of only 0.6-0.9 nm depending on solvent. Thus, based upon these data PCHD with high 1,4 content is only slightly less flexible than polystyrene. Additional studies on the chain conformation of PCHD as a function of microstructure are in progress.

Table 11: Intrinsic viscosities of PCHD in THF and chloroform

		THF	THF	Chloroform
		40°C	50°C	40°C
Sample	$M_w/10^4$	$[\eta]/\text{cm}^3\text{g}^{-1}$	$[\eta]/\text{cm}^3\text{g}^{-1}$	$[\eta]/\text{cm}^3\text{g}^{-1}$
KH-1	1.85	20.2	19.3	29.4
KH-2	1.71	18.8	18.4	28.5
KH-3	1.17	15.7	15.1	22.1
KH-4	0.55	11		13.5
KH-5	0.248	7.12		8.48

5.6 Morphology of Ring Diblock Copolymers

The effect of cyclic architecture on morphology was investigated using a series of materials synthesized by Prof. Hadjichristidis (Univ. Athens). This series consisted of five pairs of PS-PI-PS based materials. Each pair, as illustrated in Figure 12, includes a PS-PI-PS triblock and a cyclic version of that same triblock. This allows direct comparison of morphology and domain size between cyclic and linear materials with the same molecular weight and component volume fractions. TEM and SAXS was used to determine sample morphologies and domain sizes. The results are given in Table 12, and they show a consistent trend. The difference between cyclic and linear architecture leads to differences in domain size and in two cases to differences in morphology. These observations are consistent with the concept that connecting the two PS arms to form a loop decreases the tendency to curve toward the PS side of the interface or increases the tendency to curve away from this side of the interface.

Figure 12: Linear PS-PI-PS triblock and corresponding PS-PI cyclic diblock



Table 12: Morphological Results on Cyclic Diblocks and Corresponding Linear Triblocks

Sample	Vol% of PS	q^* (\AA^{-1})	$d = 2\pi/q^*$	Morphologies
Cyl 4505	10.8	0.0170	36.9	Random PS Spheres
Tri 4505	10.6	0.0180	34.9	Random PS Spheres
Cyl 4020	24.0	0.0151	41.6	PS Cylinders
Tri 4020	23.9	0.0175	35.9	PS Cylinders
Cyl 2822	37.8	0.0160	39.2	Lamellae
Tri 2822	39.5	0.0156	40.2	PS Cylinders
Cyl 2228	51.2	0.0204	30.8	Lamellae
Tri 2228	51.4	0.0180	34.9	Lamellae
Cyl 1535	69.6	0.0180	34.9	PI Cylinders
Tri1535	70.2	0.0127	49.5	Bicontinuous

(6) List of Publications and Presentations

(6a) Papers published in peer-reviewed journals

1. "Tetrafunctional Multigraft Copolymers as Novel Thermoplastic Elastomers", R. Weidisch, S. P. Gido, D. Uhrig, H. Iatrou, J. Mays, and N. Hadjichristidis, *Macromolecules*, 34, 6333 (2001).
2. "Phase Behavior of I2S Single Graft Copolymer/Homopolymer Blends", L. Yang, S. P. Gido, J. W. Mays, S. Pispas, and N. Hadjichristidis, *Macromolecules*, 34, 4235-43 (2001).
3. S. P. Gido, "Block Copolymers: Morphological Characterization," *Encyclopedia of Materials Science and Technology*, T. P. Lodge and E. J. Kramer, editors. Elsevier: **2001**, 733-739.
4. L. Yang, S. Hong, S. P. Gido,* G. Velis and N. Hadjichristidis,* "I₅S Miktoarm Star Block Copolymers," Packing Constraints on Morphology and Discontinuous Chevron Tilt Grain Boundaries," *Macromolecules* **2001**, *34*, 9069-9073.
5. D. M. Crawford,* E. Napadensky, N. C. Beck Tan, D. A. Reuschle, D. A. Mountz, K. A. Mauritz, K. S. Laverdure, S. P. Gido, W. Liu and B. Hsiao, "Structure/property relationships in polystyrene—polyisobutylene—polystyrene block copolymers," *Elsevier Thermochimica acta* **2001**, 125

6. "Living Anionic Polymerization", K. Hong, D. Uhrig, and J. W. Mays, Invited Article for the Encyclopedia of Materials: Science and Technology, 313-318 (2001).
7. "1,3-Cyclohexadiene Polymers III. Synthesis and Characterization of Poly(1,3-cyclohexadiene-block-styrene)", K. Hong and J. W. Mays, Macromolecules, **34**, 3540-47 (2001).
8. "1,3-Cyclohexadiene Polymers II. Near-Monodisperse Star and Star-block Polymers Based on Poly(1,3-cyclohexadiene), K. Hong, Y. Wan, and J. W. Mays, Macromolecules, **34**, 2482-2487 (2001).
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11. "Synthesis of Combs, Centipedes, and Barbwires: Poly(isoprene-graft-styrene) Regular Multigraft Copolymers with Trifunctional, Tetrafunctional, and Hexafunctional Branch Points", D. Uhrig and J. W. Mays, Macromolecules, **35**, 7182-7190 (2002).
12. N. P. Balsara, C. M. Marques, B. A. Garetz, M. C. Newstein and S. P. Gido, "Anisotropy of Lamellar Block Copolymer Grains," *Physical Review E* **2002**, 66 article #052802.
13. Yuqing Zhu, Roland Weidisch, Samuel P. Gido, Gabriel Velis and Nikos Hadjichristidis,* "Morphologies and Mechanical Properties of a Series of Block-Double-Graft Copolymers and Terpolymers," Macromolecules **2002**, 35, 5903-5909.
14. M. Y. Chang, F. M. Abuzaina, W. G. Kim, J. P. Gupton, B. A. Garetz, M. C. Newstein, N. P. Balsara, L. Yang, S. P. Gido, R. E. Cohen, Y. Boontongkong, and A. Bellare, "Analysis of Grain Structure in Partially ordered Block Copolymers by Depolarized Light Scattering and Transmission Electron Microscopy," Macromolecules **2002**, 35, 4437-4447.
15. Y. Zhu, S. P. Gido,* M. Moshakou, J. Iatrou, N. Hadjichristidis,* "Effect of Junction Point Functionality on the Lamellar Spacing of Symmetric Miktoarm Star Block Copolymers (PS)_n(PI)_n," Macromolecules **2003**, 36, 5719-5724.
16. "Effect of Molecular Architecture on Dynamics of Multigraft Copolymers: Combs, Centipedes, and Barbwires", J. Mijovic, M. Sun, S. Pejanovic, and J. W. Mays, Macromolecules, **36**, 7640-51 (2003).
17. "Utility of Interaction Chromatography for Probing Structural Purity of Model Branched Block Copolymers", S. Park, D. Cho, K. Im, T. Chang, D. Uhrig, and J. W. Mays, Macromolecules, **36**, 5834 (2003).

18. “Graft Copolymers”, J. W. Mays and S. P. Gido, invited article for the *McGraw-Hill Yearbook of Science and Technology* 2003, 163-66 (2003).
19. Y. Zhu, S. P. Gido, H. Iatrou, N. Hadjichristidis,* and J. Mays, “Microphase-Separation of Cyclic Block Copolymers of Styrene and Butadiene and of Their Corresponding Linear Triblock Copolymers,” *Macromolecules* **2003**, *36*, 148-152.
20. “Synthesis and Structure – Property Relationships for Regular Multigraft Copolymers”, J. W. Mays, D. Uhrig, S. Gido, Y. Zhu, R. Weidisch, H. Iatrou, N. Hadjichristidis, K. Hong, F. Beyer, R. Lach, and M. Buschnakowski, *Macromol. Symp.*, **215**, 111-126 (2004).
21. “Experimental Design and Molecular Modeling of Novel Graft Copolymers”, B. G. Sumpter, J. W. Mays, D. W. Noid, S. P. Gido, and R. Weidisch, *Polymer News*, invited Feature Article, **29**, 302-310 (2004).
22. “Interfacial Tension in Binary Polymer Blends in the Presence of Block Copolymers: Effects of Additive Architecture and Composition”, H. Retsos, S. H. Anastasiadis, S. Pispas, J. W. Mays, N. and Hadjichristidis, *Macromolecules*, **37**, 524-37 (2004).

(6b) Papers published in non-peer-reviewed journals or in conference proceedings

1. “Synthesis of Multistyrenic Aromatic Compounds”, W. A. Cristofoli, D. Uhrig, and J. W. Mays, presented at the American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.
2. “Anionic Polymerization of Styrene and 1,3-Cyclohexadiene”, K. Hong and J. W. Mays, presented at the American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.
3. “Gyroid Single Crystal Diffraction“ L. Yang, S. Hong, S. P. Gido. *Bulletin of the American Physical Society* 2001, *46(1)*, D40.136.
4. “T-Junction Grain Boundaries in Block Copolymer-Homopolymer Blends “ S. P. Gido, and E. Burgaz. *Bulletin of the American Physical Society* 2001, *46(1)*, C18.013.
5. “Effect of central junction point of AnBn star block copolymers on chain conformation in the strong segregation limit “ Y. Zhu, S. P. Gido, M. Moshakou, H. Iatrou, N. Hadjichristidis. *Bulletin of the American Physical Society* 2001, *46(1)*, C18.003.

7. "Mass Transport within Block Copolymer: The Relationship with Morphology and Grain Structure " K. S. Laverdure, S. P. Gido, B. Garetz, N. Balsara. *Bulletin of the American Physical Society* 2001, *46(1)*, D40.088.
8. E. Burgaz, S. P. Gido. "Cylinder Nucleation at T-Junction Grain Boundaries in Lamellar Block Copolymer / Homopolymer Blends" *Bulletin of the American Physical Society* 2002, *47*, B33.038.
9. Yuqing Zhu, Samuel P. Gido, Gabriel Velis, Nikos Hadjichristidis "Morphologies and tensile properties of Block-Double-Graft Copolymers" *Bulletin of the American Physical Society* 2002, *47*, B33.039.
10. "Solution Properties of 1,3-Cyclohexadiene Polymers", K. Hong and J. W. Mays, presented at the National American Chemical Society Meeting, Boston, MA, August 18 – 22, 2002. See also Polymer Preprints, 43(2), 1011-1012 (2002).
11. "Molecular Modeling of Novel Graft Copolymers", B. G. Sumpter, D. W. Noid, and J. W. Mays, presented at the National Meeting of the American Chemical Society, New Orleans, LA, March 23 – 27, 2003; see also PMSE Preprints, 88, 361-62 (2003).
12. "Structure and Scaling of Brushes Formed from Branched Polymer Amphiphiles", P. Tian, J. Yang, J. Mays, and S. M. Kilbey, presented at the National Meeting of the American Chemical Society, New Orleans, LA, March 23 – 27, 2003; see also Polymer Preprints, 44(1), 443-44 (2003).
13. "Sulfonation of 1,3-Cyclohexadiene Polymers: A New Synthetic Polyelectrolyte", K. Hong, M. Liu, and J. W. Mays, presented at the New York National Meeting of the American Chemical Society, New York, NY, September 6-11, 2003; see also, Polymer Preprints, 44(2), 657-58 (2003).
14. "Radius of Gyration of Polystyrene Combs and Centipedes in a Theta Solvent", K. Terao, B. S. Farmer, Y. Nakamura, H. Iatrou, K. Hong, and J. W. Mays, presented at the American Chemical Society Meeting, Anaheim, CA, March 28 – April 1, 2004. See also, Polym. Preprints, 45(1), 947 (2004).
15. "Effect of Molecular Architecture on Dynamics of Multigraft Copolymers", M. Sun, J. Mijovic, and J. W. Mays, presented at the National American Chemical Society Meeting, Philadelphia, PA, August 22-26, 2004. See also: PMSE Preprints, 91, 1024 (2004).

(6c) Papers presented at meetings, but not published in conference proceedings

1. "Synthesis of Regular Multigraft Poly(Isoprene-g-Styrene) with Hexafunctional

Branch Points, “Barbwires”, D. Uhrig, and J.W. Mays, presented at the IUPAC Symposium on Ionic Polymerization and Related Processes, Heraklion, Crete, Oct. 22-26, 2001.

2. “Synthesis of Model Block Copolymers”, J. W. Mays, Army Workshop on Perm-Selective Membranes, Aberdeen, MD, November 14-15, 2001.

3. “Transport Properties of Block Copolymers of Controlled Morphology”, S. P. Gido, Army Workshop on Perm-Selective Membranes, Aberdeen, MD, November 14-15, 2001.

4. “Synthesis and Properties of Linear and Branched Polymers and Copolymers Based on 1,3 Cyclohexadiene”, J. Mays and Kunlun Hong, presented at the IUPAC Symposium on Ionic Polymerization and Related Processes, Heraklion, Crete, Oct. 22-26, 2001.

5. “Synthesis of Multistyrenic Aromatic Compounds”, W. A. Cristofoli, D. Uhrig, and J. W. Mays, presented at the American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

6. “Anionic Polymerization of Styrene and 1,3-Cyclohexadiene”, K. Hong and J. W. Mays, presented at the American Chemical Society National Meeting, San Diego, CA, April 1-5, 2001.

7. “Anionic Polymerization of 1,3-Cyclohexadiene”, K. Hong and J. W. Mays, presented at the Gordon Research Conference on Polymers, Ventura, CA, January 7-11, 2001.

8. Martin-Luther Universitat Halle Wittenberg, Institut fur Werkstoffwissenschaft, June 26, 2001. Halle, Germany. *Effect of molecular architecture on transport and mechanical properties of model graft copolymers.* S. P. Gido, R. Weidisch, J. W. Mays.

9. “Effect of Controlled Molecular Architecture on Block and Graft Copolymer Morphology and Properties”, S. P. Gido, presented at the IUPAC Symposium on Ionic Polymerization and Related Processes, Heraklion, Crete, Oct. 22-26, 2001.

10. S. P. Gido. Symposium on “Polymer Interfaces and Thin Films” Materials Research Society National Meeting, November 26, 2001. Boston, Massachusetts, *Crystallographic Registry in Coil-Crystalline Block Copolymer Thin Films.*

11. IUPAC International Symposium on Ionic Polymerization, October 22-26, 2001. Crete, Greece, *Effect of controlled molecular architecture on block copolymer morphology.*

12. Polymers East Gordon Research Conference, July 8-14, 2001. Colby Sawyer College, New London, New Hampshire, invited speaker, *Crystallographic Registry in Coil-Crystalline Block Copolymers.*

13. Martin-Luther Universitat Halle Wittenberg, Institut fur Werkstoffwissenschaft, June 26, 2001. Halle, Germany, *Effect of molecular architecture on transport and mechanical properties of model graft copolymers*.
14. “Alphabet Soup with Polymers”, J. W. Mays, award lecture for the 2001 Caroline P. and Charles W. Ireland Award for Scholarly Distinction, May 15, 2001, The Club, Birmingham, AL.
15. “New Functional Nanostructured Materials Through Anionic Polymerization”, J. W. Mays, Presented to the Department of Chemistry, University of Tennessee, Knoxville, TN, May 24, 2001.
16. “New Functional Nanostructured Materials Through Anionic Polymerization”, J. W. Mays, presented at Oak Ridge National Laboratory, May 25, 2001, Oak Ridge, TN.
17. “Controlled Architecture Poly(cyclohexadiene) Polymers and Copolymers”, J. W. Mays, presented at the Department of Chemistry, University of Athens, Athens, Greece, June 13, 2001.
18. “New Functional Nanostructured Materials Through Anionic Polymerization”, J. W. Mays, presented at CEA – Saclay, Saclay, France, June 20, 2001
19. “Synthesis and Properties of Linear and Branched Polymers and Copolymers Based on 1,3 Cyclohexadiene”, J. Mays and Kunlun Hong, presented at the IUPAC Symposium on Ionic Polymerization and Related Processes, Heraklion, Crete, Oct. 22-26, 2001.
20. “Synthesis of Regular Multigraft Poly(Isoprene-g-Styrene) with Hexafunctional Branch Points, “Barbwires”, D. Uhrig, and J.W. Mays, presented at the IUPAC Symposium on Ionic Polymerization and Related Processes, Heraklion, Crete, Oct. 22-26, 2001.
21. “Synthesis of Model Block Copolymers”, J. W. Mays, Army Workshop on Perm-Selective Membranes, Aberdeen, MD, November 14-15, 2001.
22. “Anionic Polymerization: Squeezing Something New Out of an Old Technique”, J. W. Mays, presented at the Department of Polymer Science and Engineering, Univ. of Massachusetts, Amherst, MA, December 14, 2001.
23. “Nanostructured Soft Materials through Block Copolymer Self-Assembly”, J.W. Mays, presented at Battelle Technical Council Meeting Georgia Institute of Technology, Atlanta GA, March 4-6, 2002.
24. “A Block Copolymer Approach to Novel Nanotubes”, K. Hong, J.Zhu, S. Gido, T. Russell and J.W. Mays, presented at Battelle Technical Council Meeting Georgia Institute of Technology, Atlanta GA, March 4-6, 2002.
25. “Nanostructured Soft Materials through Block Copolymer Self-Assembly”, J.W.

Mays, presented at Battelle Technical Council Meeting Georgia Institute of Technology, Atlanta GA, March 4-6, 2002.

26. “The Utility of Model Polymers in Understanding Structure-Property Relationships for Complex Polymers”, J. W. Mays, presented at the International Symposium on Polymer Analysis and Characterization, Twente University, The Netherlands, June 17-19, 2002.

27. “New Branched Polymer Architectures and New Monomers in Anionic Polymerization”, J. W. Mays, presented at Bridgestone/Firestone Research Center, Akron, OH, July 9, 2002.

28. S. P. Gido. Institut für Polymerforschung Dresden, Germany. September 12, 2003. *Effect of Controlled Molecular Architecture on Block and Graft Copolymer Morphology and Properties*

29. S. P. Gido. Elastomers Gordon Research Conference, June 29-July 4, 2003. Colby Sawyer College, New London, New Hampshire. Invited Speaker, *Multigraft Copolymers of Well Defined Molecular Architecture as Novel Thermoplastic Elastomers*.

30. “Tailoring Macromolecular Architecture with Anionic Polymerization: The Need for Rigorous Molecular Characterization”, J. W. Mays, presented at the Workshop on Polymer Synthesis for Physicists, American Physical Society Meeting, Austin, TX, March 1-2, 2003.

31. “Morphologies and Tensile Properties Study on Multigraft Copolymers with Tri-, Tetra-, and Hexafunctional Branch Points”, R. Weidisch, Y. Zhu, E. Burgaz, S. P. Gido, D. Uhrig, and J. W. Mays, presented at the American Physical Society Meeting, Austin, TX, March 3-7, 2003.

32. “Synthesis and Structure – Property Relationships of Model Graft Copolymers”, J. W. Mays, invited plenary lecture at the Molecular Architecture for Performance (MAP) MURI Workshop (DOD), Aberdeen, MD, May 27 – 28, 2003.

33. “Model Graft Copolymers”, J. W. Mays, presented at Kraton Polymers, Houston, TX, June 18, 2003.

34. “Synthesis and Structure-Property Relationships for Regular Multigraft Copolymers”, J. W. Mays, invited talk at the IUPAC-Sponsored International Symposium on Ionic Polymerization, Boston, MA, June 30 – July 4, 2003.

35. “Synthesis of Hyperbranched Polybutadiene through Anionic Self-Condensing Vinyl Polymerization”, D. Baskaran and J. W. Mays, presented at the IUPAC-Sponsored International Symposium on Ionic Polymerization, Boston, MA, June 30 – July 4, 2003.

36. "Synthesis and Properties of Poly(isoprene-graft-styrene) Regular Multigrafts", R. Weidisch, S. P. Gido, D. Uhrig, and J. W. Mays, presented at the 26th Annual Australian Polymer Symposium, Noosa, Australia, July 14-16, 2003.
37. "Synthesis and Properties of Homopolymers and Copolymers having Multiple Regularly Spaced Branch Points", J. W. Mays, presented at the Canadian Society for Chemistry Meeting, Ottawa, August 10-14, 2003.
38. "Synthesis and Properties of Homopolymers and Copolymers having Regularly Spaced Multiple Branch Points", J. W. Mays, presented at IPF, Dresden, Germany, September 11, 2003.
39. "Solution Properties of Model Branched Polymers", J. W. Mays, plenary lecture at Wyatt Technology Light Scattering Colloquium, Santa Barbara, CA, September, 22, 2003.
40. "Synthesis and Properties of Long Chain Branched Polymers and Copolymers", J. W. Mays, invited seminar presented to the Department of Chemistry, Virginia Tech, October 15, 2003.
41. "Synthesis and Characterization of Sulfonated 1,3-Cyclohexadiene Polymers", presented at Gordon Research Conference on Colloidal, Macromolecular and Polyelectrolyte Solutions, Ventura, CA Feb.1-6, 2004.
42. "Influence of Molecular Architecture on the Tensile Properties of Multigraft Copolymers", R. Weidisch, R. Lach, Y. Zhu, E. Burgasz, S. Gido, D. Uhrig, J. Mays, and N. Hadjichristidis, presented at the American Physical Society Meeting, Montreal, Canada, March 22 – 26, 2004.
43. "Defect Study on Noncentrosymmetric Lamellar Block Copolymer Blends", S. Chen, S. P. Gido, T. Tsoukatos, A. Avgeropoulos, N. Hadjichristidis, K. Hong, and J. W. Mays, presented at the American Physical Society Meeting, Montreal, Canada, March 22 – 26, 2004.
44. "Solution Properties of Regular Comb and Centipede Polystyrenes Under Good Solvent and Theta Solvent Conditions", J. W. Mays, invited talk at the International Workshop on Branched Polymers for Performance, Williamsburg, VA, May 23 -26, 2004.
45. "On-line Measurement of Molecular Weight and Radius of Gyration of Polystyrene in a Good Solvent and in a Theta Solvent Measured with a Two-Angle Light Scattering Detector", K. Terao and J. W. Mays, presented at the International Symposium on Polymer Analysis and Characterization, Heidelberg, Germany, June 7-9, 2004.
46. "New Model Polyelectrolytes", K. Hong, P. Britt, D. Holley, J. Yang, and J. Mays, invited presentation at Polyelectrolytes 2004, Amherst, MA, June 14-18, 2004.

47. “New Charged Block Copolymers Based on Poly(cyclohexadiene)”, K. Hong, P. Britt, and J. W. Mays, presentation at Polyelectrolytes 2004, Amherst, MA, June 14-18, 2004.

48. “Morphology and Mechanical Properties of Multigraft Copolymers”, U. Staudinger, R. Weidisch, S. P. Gido, D. Uhrig, J. Mays, H. Iatrou, and N. Hadjichristidis, 40th World Polymer Congress MACRO 2004, Paris, France, July 4 – 9, 2004.

(6d) Manuscripts submitted, but not published

1. “Radius of Gyration of Polystyrene Combs And Centipedes in a Theta Solvent”, K. Terao, B. S. Farmer, Y. Nakamura, H. Iatrou, K. Hong, and J. W. Mays, *Macromolecules*, submitted (2004).

2. “Role of Branching on the Structure of Polymer Brushes Formed from Comb Copolymers”, P. Tian, D. Uhrig, J. W. Mays, H. Watanabe, and S. M. Kilbey II, *Macromolecules*, submitted (2004).

(6e) Technical Reports Submitted to ARO

1. Interim Progress Report 2001
2. Interim Progress Report 2002
3. Interim Progress Report 2003

(7) Scientific personnel supported by this project and honors / awards / degrees received

University of Tennessee at Knoxville

Jimmy Mays, Distinguished Professor, University of Tennessee; Distinguished Scientist, Oak Ridge National Lab.

Mays Honors/Awards

Mays was the 2001 Recipient of the Caroline P. and Charles W. Ireland Prize for Scholarly Distinction (UAB’s highest award to faculty in arts and sciences). Also in 2001 he was named University Scholar at UAB (honorary faculty status granting maximum latitude in conducting interdisciplinary teaching and research). Mays was a 2003 Recipient of the Arthur K. Doolittle Award of the Polymeric Materials Science and Engineering Division of the American Chemical Society. Distinguished Professor, University of Tennessee; Distinguished Scientist, Oak Ridge National Lab.

David Uhrig (received PhD in 2002)

George Sakkellariou (received PhD in 2003)

Kunlun Hong, Postdoc – now staff member at ORNL

Dr. Helen Haining Ji, Ph.D. 2001, Received further support as a postdoc.

University of Massachusetts at Amherst

Samuel P. Gido, Associate Professor

Gido Honors/Awards

The Mettler Toledo Thermal Analysis Education Award in Honor of Prof. Edith A. Turi. 2002.

Dr. Michael Lizhang Yang, Ph.D. 2001. Currently at 3M, Austin, Texas.

Dr. Kenneth Laverdure, Ph.D. 2001. Currently at Dow Chemical, Freeport, TX.

Jane Yuqing Zhu, Ph.D. 2003., Currently at Eastman Chemical, Kingsport, TN.

Mr. Engin Burgaz, Doctoral Student. Ph.D. expected in 2005.

(8) “Report of inventions” (by title only)

None

(9) Technology transfer

We have interacted with Scientists at the Army Research Laboratory (Aberdeen, MD) on this research. Additionally we have provided morphological characterization support (Gido) and synthetic support (Mays) for internal ARL projects. We have interacted on the SABRE project in which ARL scientists are working to prepare permselective membranes based on block copolymers. We worked with Triton Systems on a SBIR program to develop improved barrier materials for military use (based on SABRE concept developed in this program). This involved Dawn Crawford and Jim Sloan of ARL.

Under this grant Mays is synthesizing block copolymers for Army scientists at the Natick RD&E Center.

The super-elastomers developed in this program have attracted much attention. Mays was invited to Bridgestone/Firestone and to Kraton Polymers to lecture on the synthesis and properties of these materials. Our collaborator on the mechanical properties of these materials, Dr. Roland Weidisch of Institute for Polymer Research in Dresden Germany has received an innovation award from the German government based on our joint work.

Dr. Mark Mezger of Picatinny Arsenal twice visited the University of Tennessee in 2004 to discuss developing a research relationship between UT and ARDEC at Picatinny for the purpose of development of science and technology for soldier protection.

Gido has use expertise in the morphological characterization of PS-PIB block copolymers obtained through collaborating with ARL scientists on SABRE to help a company (Boston Scientific Inc., Natick, Massachusetts) better understand their polymer coated heart stents.